Effect of cobalt additions on the properties of 5N red gold alloys

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Introduction

A wide range of carat gold alloys with different gold contents (1) enables the various needs of jewellery production to be satisfied with regard to both the manufacturing operations and the characteristics required for the finished product. Therefore, chemical composition has a fundamental importance for the evaluation of a gold alloy, and the presence of alloying elements or of impurities can have a favourable effect on some properties and an adverse effect on others (2).

The jewellery manufacturing process may require the manufacture of semi-finished products by means of the traditional processes involving plastic deformation or may require the use of investment casting, also known as the ‘lost-wax’ process (3). In the case of cold working, material workability is strongly influenced by the composition and by the tendency to work harden. Work hardening should be taken into consideration because it can hinder cold working operations, but it can also be advantageously used to increase jewellery strength (4). It is well known that annealing can eliminate the effect of work hardening and restore the workability of the material (5).

Alloy microstructure and, particularly, grain size have a fundamental importance for the workability of the material and for the good appearance of the finished product. Before annealing, the alloy should be subjected to a sufficient amount of plastic cold deformation, i.e. the critical amount of deformation should be attained. In this way, the number of nucleation sites for the growth of new crystal grains during recrystallisation is adequate to obtain a sufficiently fine grained structure. Otherwise, the recrystallising grains will grow too big, and defects such as an ‘orange peel’ surface will arise in the subsequent manufacturing operations.

Most carat gold alloys are based on the Au-Ag-Cu ternary system. The colour of the alloys is affected by the composition, including the addition of other alloying elements such as zinc and nickel (6, 7). In particular, when copper content is high, the alloys show a red tinge or colouration.

Red gold alloys are widely used, because the red tinge gives them a pleasant appearance and they can be worked with normal cold working techniques or melted and cast. High copper content alloys can be more valuable, thanks to their appearance, but sometimes the high copper content can give problems of workability that can be ascribed to an excessive grain growth.

In the present work, we have carried out cold rolling and heat treatment tests, in order to get a deeper knowledge of some phenomena related to the workability of 5N red gold alloys*. The microstructures of the samples produced have been examined and the mechanical properties determined.

Two different alloys have been tested: a quaternary gold-silver-copper-zinc (Au-Ag-Cu-Zn) 5N 18 carat alloy and a similar one with a 0.5% cobalt addition, denoted as 5N 0.5% Co alloy. In this way, we wanted to verify the effectiveness of the grain refining effect of cobalt in the case of 5N alloys. Data from the technical literature (8) on the effect of different alloying elements on the structural properties of a 3N alloy, show that a 0.5% Co addition has given the best results for grain refining.

Experimental

13 kg of 75% gold alloy have been used for the tests. Two melting and casting techniques have been used: ingot casting and continuous casting. For ingot casting, the alloys were melted under an argon atmosphere and ingots with 50 x 35 mm or 50 x 20 mm cross section have been cast in metallic moulds. In the case of continuous casting, melting was carried out under nitrogen and a bar, with rectangular cross section of 15 x 39 mm, cast in a graphite mould.

Table 1. Composition of the alloys

Alloy	Au %wt	Ag %wt	Cu %wt	Zn %wt	Co %wt
5N standard	75.0	4.2	20.3	0.5	-
5N 0.2% Co	75.0	4.2	20.1	0.5	0.2
5N 0.5% Co	75.0	4.0	20	0.5	0.5

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*Editor's Note: The ‘N’ series of alloys are the European colour standards for 14 and 18 carat golds, covered under the European Standard EN 28654 and the International Standard ISO 8654. The Alloy Data Sheet for 5N red 18 carat gold is given on page 14 of reference 7]

A standard alloy and two additional alloys with increasing cobalt additions were produced. The compositions of the alloys are shown in Table 1 and samples of each were subjected to differential thermal analysis (DTA) to determine the effect of cobalt on thermal properties. On the basis of the results obtained, subsequent work was only carried out on the standard alloy and the alloy with the 0.5% Co addition.

Metallographic examination of the cast products was carried out to observe the structure differences produced by the different casting processes. Both materials were then cold rolled with the same cycle of plastic deformation. The tests were performed in such a way as to monitor the evolution of structure and mechanical properties during the whole deformation cycle. In each rolling pass, the material was subjected to a deformation of 15% reduction, and a sample taken for metallographic examination, hardness measurement and heat treatment tests.

For solution heat treatment (annealing), the samples were held for 30 minutes in a furnace at the desired temperature and then water quenched. The annealing temperatures ranged from 250°C to a maximum in the range 550° to 700°C in 50°C steps.

Blanking tests were carried out, producing blanks for watch case production. These were then annealed to eliminate the effects of cold working. Their microstructures were examined under the optical microscope before and after annealing.

Differential Thermal Analysis

DTA was used to determine the melting range and the solid state transformation temperatures. It is necessary to know these temperatures so that the annealing and age hardening heat treatments can be performed correctly. DTA enables the phase diagram of any alloy to be determined.

From the cooling curves of the three alloys, the graphs in Figures 1 and 2 have been drawn and show the melting temperature and transformation temperature range of these alloys. It should be stressed that Figures 1 and 2 do not represent a binary phase diagram, but a section of a quaternary phase diagram: when cobalt concentration increases, the concentrations of copper and silver decrease, while the gold and zinc concentrations stay constant. Therefore, these graphs are valid only for the tested alloy compositions.

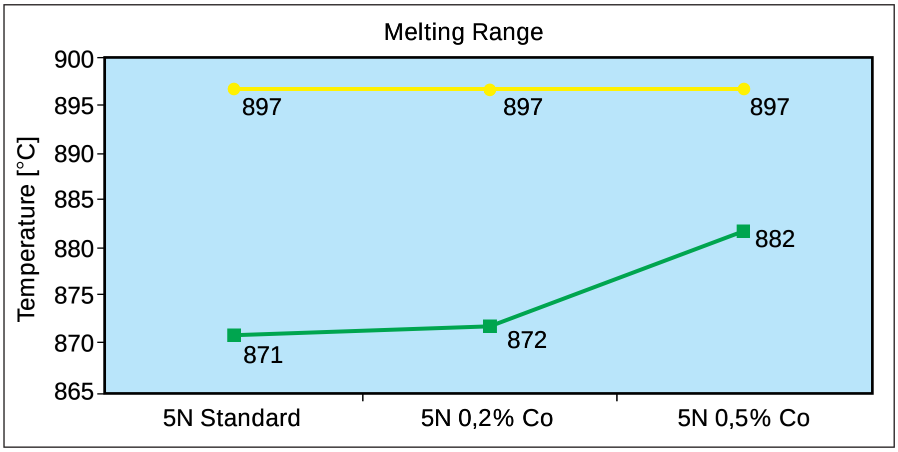

Figure 1 - Solidification temperature range of the alloys

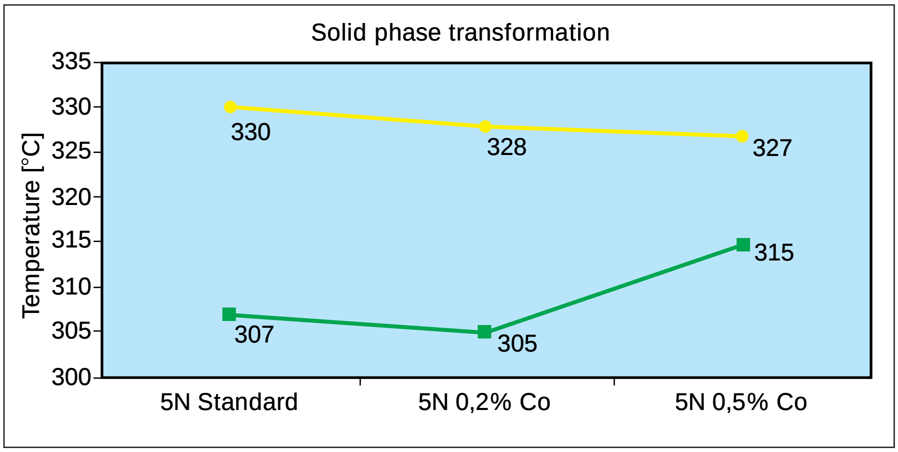

Figure 2 - Solid state transformation temperature range of the alloys

Microstructure of the cast alloys

The microstructures of the samples taken from the cast materials are shown in Figure 3. The continuously cast material shows a faintly segregated dendritic structure, with more rounded grains. This structure can be ascribed to cooling conditions: the formation of columnar grains is hindered by the geometry of the solidification front which advances from the sides to the centre and from the bottom to the top. Moreover, it is important to observe that the material stays at high temperature for some time because,

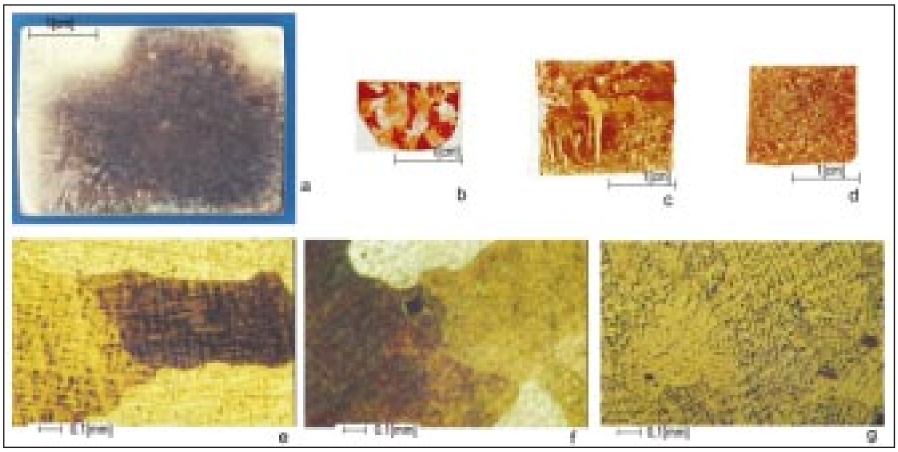

Figure 3 - As cast structures:
a) 5N standard alloy, ingot cast,
b) 5N standard alloy, continuous casting,
c) 5N 0.5% Co alloy, ingot cast,
d) 5N 0.5% Co alloy, cold worked, remelted and ingot cast,
e) enlargement of (a),
f) enlargement of (b),
g) enlargement of the structure of the 5N 0.5% Co alloy. When observed under the optical microscope, the structure of this alloy is not affected by the casting technique.

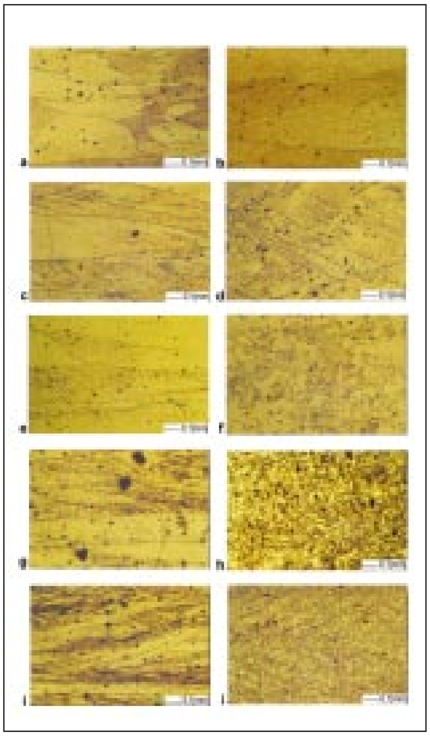

Figure 4 - Effect of cold rolling and annealing on the microstructure of 5N standard alloy. Samples annealed at 550°C for 30 minutes and water quenched:
a) 15% cold rolled
b) 15% cold rolled and annealed
c) 30% cold rolled
d) 30% cold rolled and annealed
e) 45% cold rolled
f) 45% cold rolled and annealed
g) 60% cold rolled
h) 60% cold rolled and annealed
i) 75% cold rolled
j) 75% cold rolled and annealed

after solidification, it receives heat by conduction from the liquid pool. This could allow solid state diffusion and so homogenize the material. It is evident that cobalt has acted as a grain refiner. Apparently, the structure obtained has been produced by a larger number of solidification nuclei. It should be noted that the first casting of the cobalt-containing alloy had a rather inhomogeneous structure, but this situation did not recur in the subsequent casting operations. The reason for this is not clear. In practice, the characteristics of alloys can change with remelting: it could be speculated that this phenomenon is related to an improved homogeneity of the material.

The compositions of the cast alloys were verified by means of X-ray fluorescence (XRF) analysis and were found to be the same in all casting operations. In spite of the different structures, all cast alloys behaved in the same way when rolled. So it can be concluded that the observed inhomogeneity was limited to the observed sample.

It is well known that 5N alloys require a plastic deformation of 75% reduction before blanking to obtain a structure sufficiently fine grained to prevent the orange peel effect or the brittleness that can be ascribed to a coarse grain structure. If we use a grain refiner, the working cycle can be shortened, because the optimum structure can also be obtained with a lower thickness reduction by rolling.

Effect of rolling on alloy properties

Both alloys were cold rolled to varying total thickness reductions: 15%, 30%, 45%, 60% and 75%. After each rolling step, the structures of the alloys were observed and the hardness measured to evaluate the degree of work hardening. The effect of the thickness reduction on the alloy microstructures are shown in Figures 4 and 5.

With a 15% thickness reduction, the structure is little changed: the deformation takes place only in the surface layers and grain size is relatively unchanged. Annealing does not induce because the dislocation density in the crystal lattice is not high enough: the material structure is thermodynamically stable and, under these conditions, annealing only causes grain growth. Annealing after a 15% total deformation is of little benefit because both hardness and strength do not change much. Also, rolling reductions of 30% and 45% are

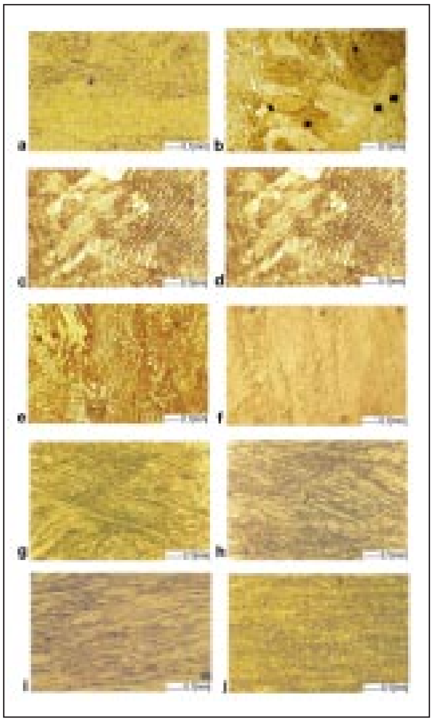

Figure 5 - Effect of cold rolling and annealing on the microstructure of 5N 0.5% Co alloy. Samples annealed at 550°C for 30 minutes and water quenched:
a) 15% cold rolled
b) 15% cold rolled and annealed
c) 30% cold rolled
d) 30% cold rolled and annealed
e) 45% cold rolled
f) 45% cold rolled and annealed
g) 60% cold rolled
h) 60% cold rolled and annealed
i) 75% cold rolled
j) 75% cold rolled and annealed

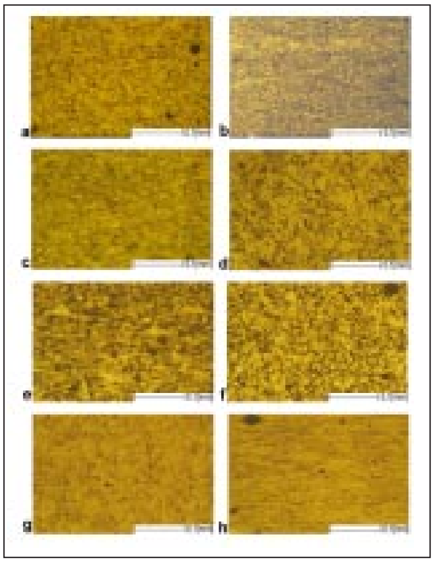

Figure 6 - Effect of cold re-rolling and annealing on the microstructure of 5N standard alloy, cold rolled to 75% reduction and annealed. Samples annealed at 550°C for 30 minutes and water quenched:
a) 15% cold re-rolled
b) 15% cold re-rolled and annealed
c) 30% cold re-rolled
d) 30% cold re-rolled and annealed
e) 45% cold re-rolled
f) 45% cold re-rolled and annealed
g) 60% cold re-rolled
h) 60% cold re-rolled and annealed

not sufficient to guarantee a good result with blanking, even though the 0.5% Co alloy has a finer microstructure. For the standard 5N alloy, a minimum thickness reduction of 75% is recommended; for the 5N 0.5% Co alloy, a 60% thickness reduction may be sufficient. This hypothesis can be verified by comparing the alloy structures shown in Figures 4 and 5.

The maximum thickness reduction level that can be tolerated by both alloys has been determined. The cast plates were cold rolled to 85% thickness reduction, but cracks were observed on the edges of the rolled sheets, hampering their use in subsequent manufacturing operations. A maximum thickness reduction of 75% is recommended for both alloys.

The material cold-rolled 75% was annealed under different conditions to determine the optimum annealing conditions (heat treatment is discussed in the following paragraph). After annealing, both alloys have been cold rolled again and the structures examined, Figures 6 and 7. In this way, a very fine grained structure has been obtained which should be suitable for all cold

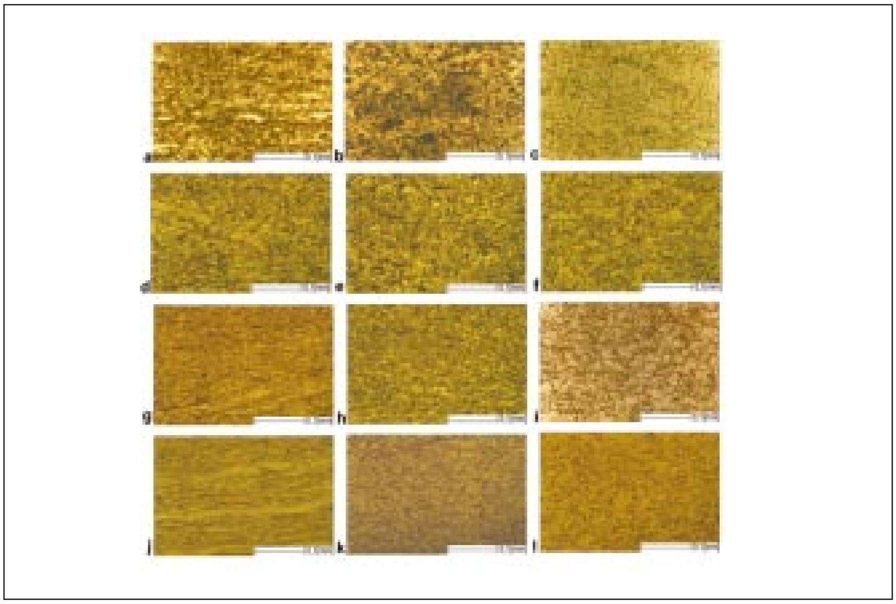

Figure 7 - Effect of cold re-rolling and annealing on the microstructure of 5N 0.5% Co alloy, cold rolled to 75% reduction and annealed at 550°C. Samples annealed at 550°C or at 700°C for 30 minutes and water quenched:
a) 15% cold re-rolled
b) 15% cold re-rolled and annealed at 550°C
c) 15% cold re-rolled and annealed at 700°C
d) 30% cold re-rolled
e) 30% cold re-rolled and annealed at 550°C
f) 30% cold re-rolled and annealed at 700°C
g) 45% cold re-rolled
h) 45% cold re-rolled and annealed at 550°C
i) 45% cold re-rolled and annealed at 700°C
j) 60% cold re-rolled
k) 60% cold re-rolled and annealed at 550°C
l) 60% cold re-rolled and annealed at 700°C

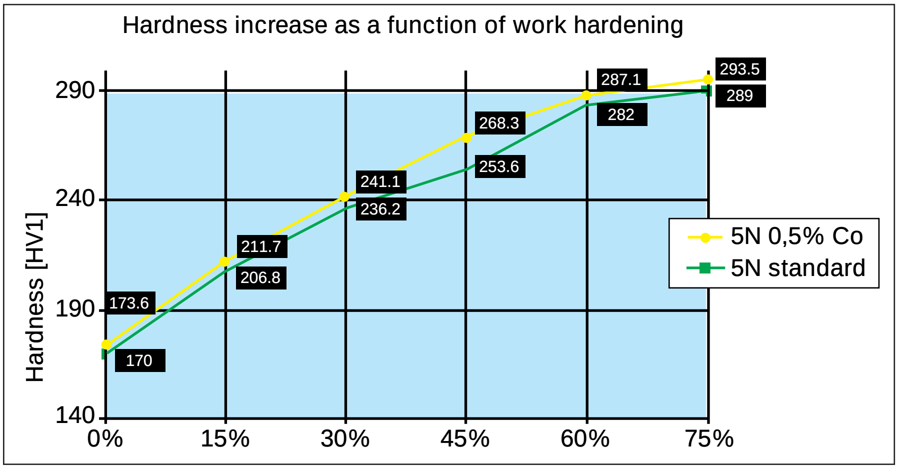

Figure 8 - Effect of cold rolling on hardness of as cast material.

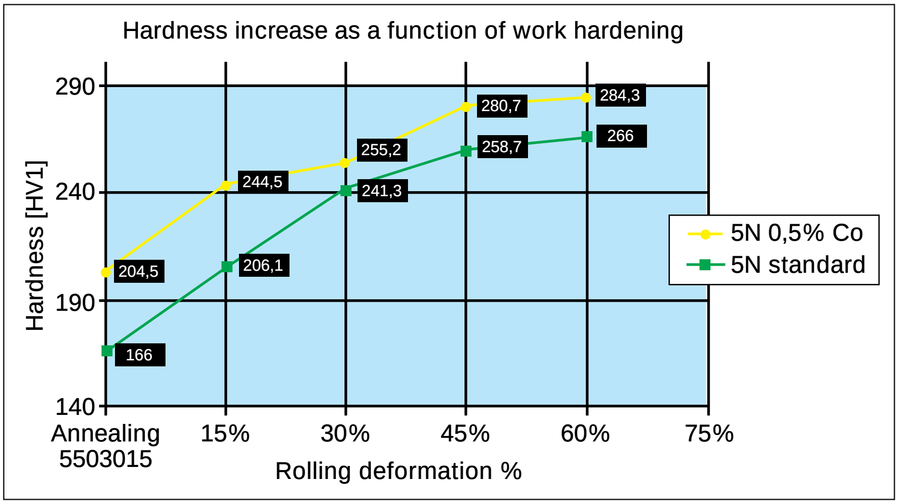

Figure 9 - Effect of cold rolling on hardness of material cold rolled to 75% reduction and annealed.

working or machining operations. However, the double rolling process is time consuming and the improvement that can be obtained, when compared with the simple 75% rolling reduction, is not such as to justify its adoption.

Plastic deformation increases dislocation density, producing an increase in hardness and tensile strength. The increase in strength produced by cold deformation, is known as work hardening and this can be measured by plotting hardness versus thickness reduction by rolling. This knowledge of alloy work hardening enables the optimum hardness of rolled sheet for various applications to be defined. For example, blanking should be carried out on a slightly work hardened material which, in the case of gold alloys, corresponds to a Vickers hardness of HV 210 to HV 240. If a graph of work hardening is available for each alloy, it should be possible to standardize the manufacturing operations and to operate under the most favourable conditions. Usually, the material is annealed and subsequently rolled with a fixed thickness reduction (about one millimetre) to give the material the required hardness. This practice can give good results, but it does not guarantee optimum conditions in all cases.

The work hardening curves are shown in Figures 8 and 9. Figure 8 shows the effect on hardness of cold rolling the cast material up to a 75% thickness reduction. Figure 9 is an extension of Figure 8: the 75% cold rolled material has been annealed at 550°C for half an hour, water quenched, and then cold rolled again. The gap between the curves of the two alloys is wider in Figure 9 because the 5N 0.5% Co alloy requires a higher annealing temperature. Consequently, it was incompletely recrystallised before subsequent rolling and thus it is harder than the 5N standard alloy. These alloys have different thermodynamic properties and their annealing temperatures are different. In this test, the alloys have been annealed at the same temperature to provide a comparison from the same standpoint.

Effect of heat treatment

For each rolling reduction, samples of the alloys have been annealed in a furnace for 30 minutes and water quenched. As already stated, the annealing temperature was increased in 50°C steps, starting from 250°C. In this way, the effect of annealing temperature on hardness has been determined, Figures 10-13.

A comparison of the curves for samples with the same rolling reduction, Figures 14 and 15, shows:

(i) The hardness of 5N 0.5% Co alloy is always higher than the hardness of the standard alloy. This can be ascribed to the effect of grain size, because a higher energy is required to activate recrystallization in the 5N 0.5% Co alloy.

(ii) The comparison of the inflexion points of the two curves shows another important difference.

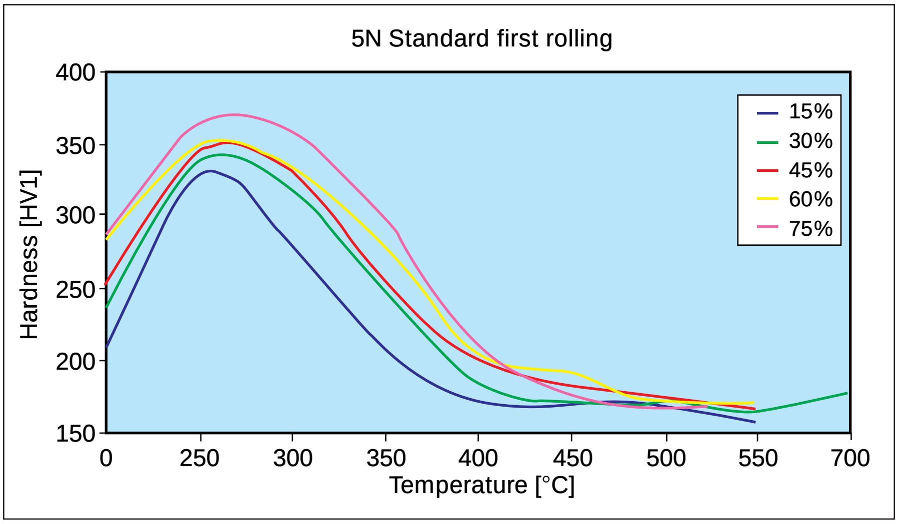

Figure 10 - Effect of increasing annealing temperature on hardness of as cast 5N standard alloy (annealing time: 30 minutes) for different levels of cold rolling reduction.

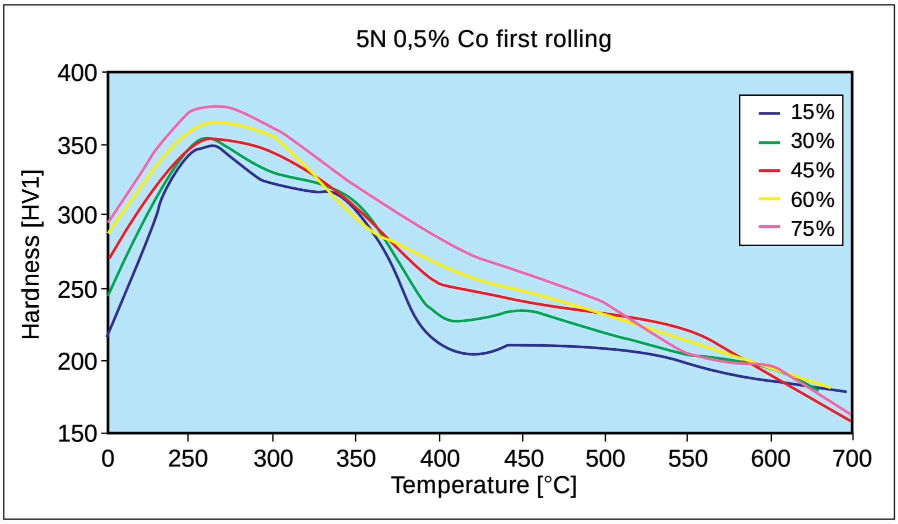

Figure 11 - Effect of increasing annealing temperature on hardness of as cast 5N 0.5% Co alloy (annealing time: 30 minutes) for different levels of cold rolling reduction.

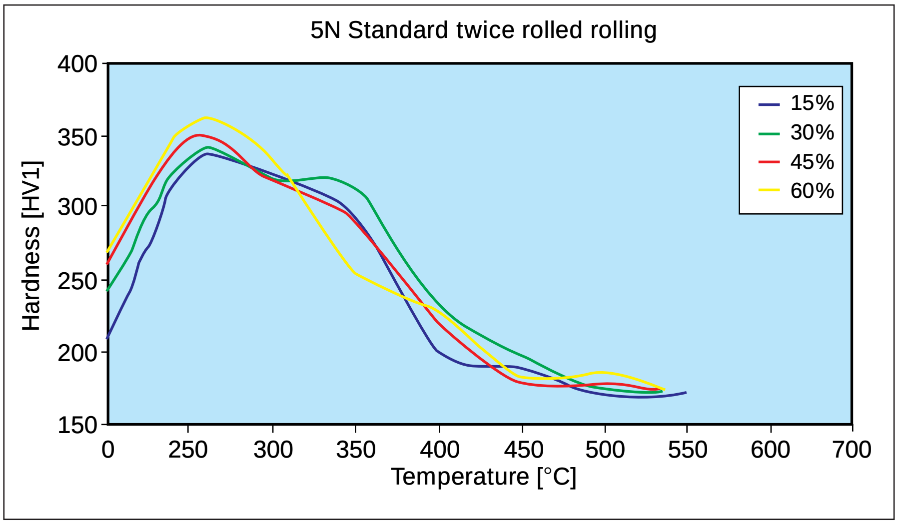

Figure 12 - Effect of increasing annealing temperature on hardness of 5N standard alloy, cold rolled to 75% reduction and annealed, for different levels of cold rolling reduction (annealing time: 30 minutes).

In the 5N standard alloy, hardness and tensile strength (these parameters can be assumed to be proportional) decrease rather sharply between 300 and 400°C. In the 5N 0.5% Co alloy, the hardness decreases almost linearly with annealing temperature; consequently materials with hardnesses in the range HV 308 - HV 160 could be obtained. This is very important because it will be possible to keep mechanical properties under control. In practice, for gold alloys, blanking cannot be performed immediately after annealing, because the metal is too soft and a slight rolling is used to obtain the required hardness increase.

(iii) The temperature where recrystallization ends and grain growth starts is 550°C for the standard alloy and higher than 650°C for the cobalt-containing alloy.

The examination of the graphs and of the microstructure of the alloys has given a very interesting result. When we combine the hardness plot for the 75% cold rolled 5N 0.5% Co alloy with the related microstructures, we obtain Figure 16, where the direct correlation between hardness and microstructure is clearly shown.

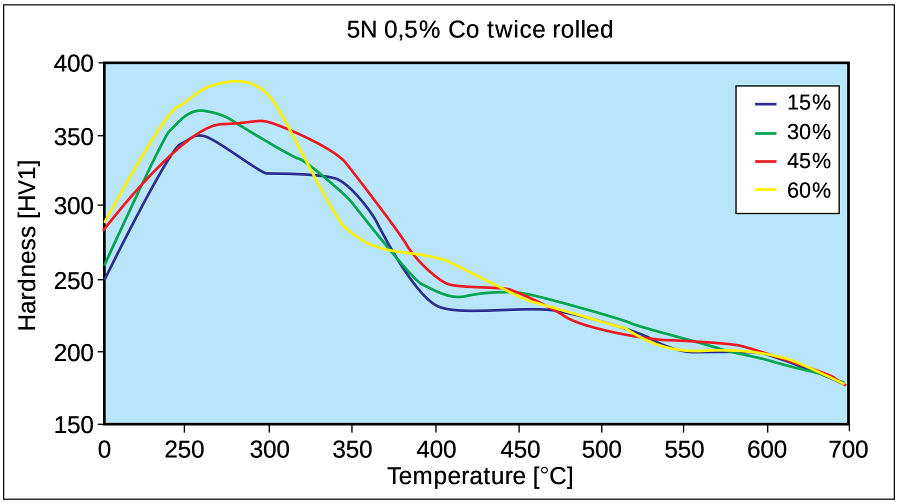

Figure 13 - Effect of increasing annealing temperature on hardness of 5N 0.5% Co alloy, cold rolled to 75% reduction and annealed, for different levels of cold rolling reduction (annealing time: 30 minutes).

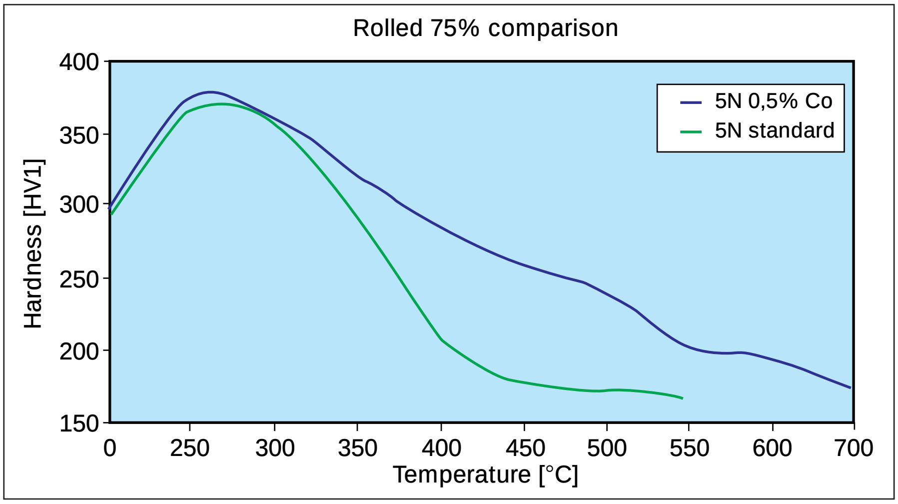

Figure 14 - Effect of annealing temperature on hardness of as cast 5N standard alloy and 5N 0.5% Co alloy, both cold rolled to 75% reduction.

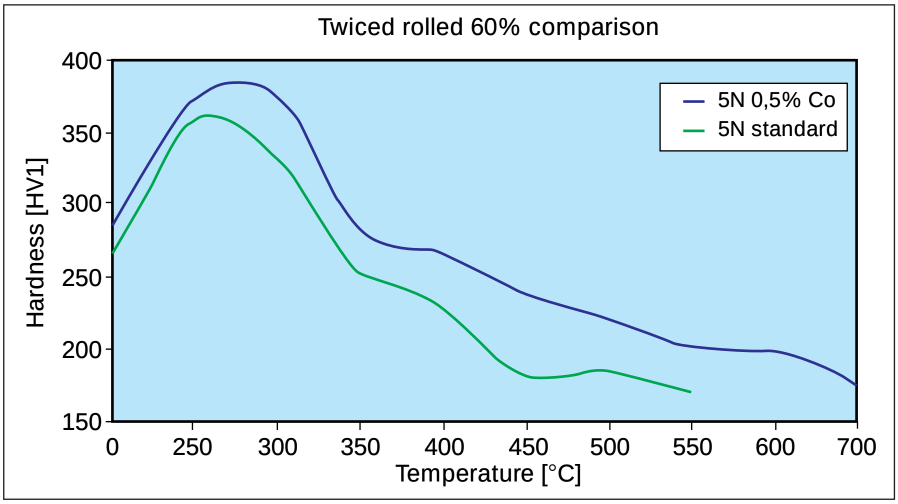

Figure 15 - Effect of annealing temperature on hardness of 5N standard alloy and 5N 0.5% Co alloy, both cold rolled to 60% reduction. Starting material: cold rolled to 75% reduction and annealed.

Age hardening

Age hardening tests have been performed to determine the highest hardness that can be obtained with the 5N 0.5% Co alloy. Samples of the 5N 0.5% Co alloy, cold rolled 75%, annealed at 700°C for 2 hours and water quenched, were aged at 250°C for times up to 54 hours, removed from the furnace and air cooled.

The results are summarized in Figure 17. It is interesting to observe that the maximum hardness, HV 344, obtained after 33 hours of ageing, is only 10% higher than the hardness obtained after 1 hour of ageing (HV 319), but it is nearly twice the hardness of the annealed sample (HV 160). Consequently, it is uneconomic to age harden for a time longer than 1 hour.

Blanking tests

After rolling, a blank for a watch case has been blanked out in a press for each alloy. The microstructures of the cross section of the watch cases are shown in Figure 18. It should be observed that blanking work hardens the structure considerably. After blanking, it is necessary to anneal the blank before drawing it. The heat treatment involves the whole piece and, consequently, includes its core zone, marked with a ‘b’ in Figure 18. It is interesting to observe the change of grain size in this core zone after annealing. In this zone there has not been any plastic deformation and so no recrystallization takes place.

For the production of watch cases, it is important to have a fine structure in the core because frequently after drawing, it is necessary to carry out machining operations. Machining brings to the surface inner zones that have been annealed many times without being subjected to any plastic deformation. Therefore, these zones may show a coarse grained structure that is difficult to polish. To prevent this problem, the starting material should preferably have a very fine grained structure, obtained either by rolling many times or by the use of a grain refiner. Examination of the four micrographs clearly shows that the structure of the cobalt-containing alloy is much finer. As we have said above, this condition is very favourable.

Other heat treatment tests

5N alloy is a special alloy in that brittle fracture can occur in some ingots during rolling of a batch produced under the same conditions. The fractures are intergranular and it is not clear why this defect occurs in some casts only. To find an explanation of this phenomenon, an ingot of 5N 0.5% Co alloy was homogenized for 2 hours at 700°C in a furnace and then quenched in water at 15°C. The aim of this heat treatment was to homogenize the structure and hence to make it more tough. The heat treated ingot was then rolled and the results are shown in Figure 19a. The rolled material is very brittle and the fractures caused by rolling are easily visible. The hardness was about HV 170, very similar to the hardness observed in the other samples. Since the fracture has not been caused by an anomalous hardness, then it can be hypothesised that it could be caused by grain boundary segregation of some impurity element or of some oxide resulting from the heat treatment.

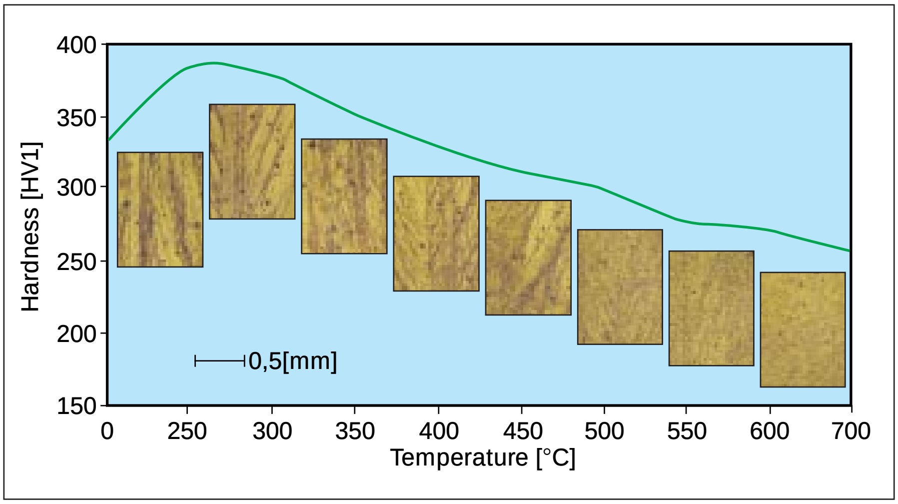

Figure 16 - Effect of annealing temperature on hardness of 5N standard alloy cold rolled to 75% reduction. The photographs show the microstructures after annealing at different temperatures.

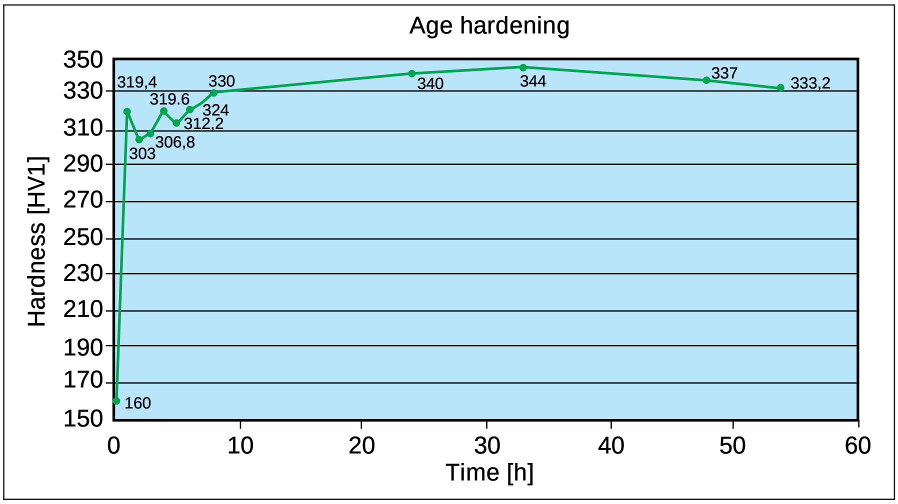

Figure 17 - Effect of ageing at 250°C on hardness of 5N 0.5% Co alloy cold rolled to 75% reduction and annealed at 700°C.

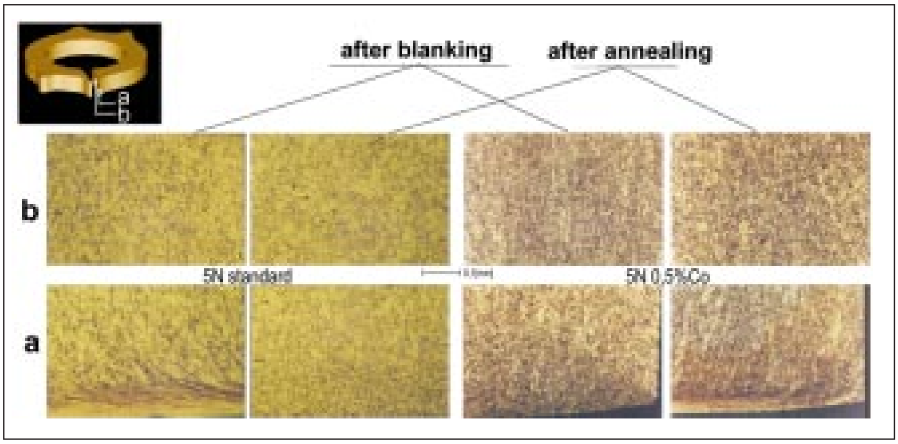

Figure 18 - Microstructure of watch cases after blanking and annealing. Comparison between 5N standard alloy and 5N 0.5% Co alloy. The samples have been taken from zone ‘b’ (core) and zone ‘a’ (surface)

The ideal condition should be to cast the alloy in a very efficiently cooled mould. Holding at high temperature should be avoided, because the diffusion coefficient depends exponentially on the temperature. The critical range is from 880° to 600°C. At lower temperatures, diffusion is much slower, but heat should still be removed rapidly, to avoid the hardening phenomena.

Investment casting

The standard 5N alloy normally shows good castability. Therefore, its castability has not been tested in this work, because this alloy is commonly used in production. Consequently, only the 5N 0,5% Co alloy has been tested. There is no standard test for castability in investment casting and, therefore, a particularly complex model has been selected, i.e. a wax grid, commonly used for manufacturing dental prostheses and in assessments of the castability of jewellery alloys. For the assessment, the completeness of filling of the form, in percent, has been measured and an empirical evaluation of the quality of the casting has been carried out by setting a gemstone. In this case, setting requires incision of the metal, to pull up a curl of metal that is pushed onto the stone to grip it. If the alloy is too brittle, the curl fractures and the setting operation fails. The result of the casting test is shown in Figure 20.

The casting test was performed in a centrifugal casting machine with a separate melting furnace. The melting temperature was determined by DTA. The flask temperature prescribed for the standard red gold alloy has been used:

Melting temperature: 897°C
Casting temperature: 920°C
Outer flask temperature: 585°C
Inner flask temperature: 667°C
Weight loss: 0 g.

The test has given very good results, and the mould has been completely filled. Stone setting has also been accomplished successfully, so it can be concluded that the 5N 0.5% Co alloy is suitable also for investment casting and stone setting.

Conclusions

The evaluation of the test results enabled a comparison of the positive and negative characteristics of both alloys which is useful in defining the respective range of use of each alloy. A wise choice of the alloy enables a reduction in manufacturing time and use of resources. This work has shown that both 5N alloys are suitable for cold working and investment casting, but their structural, thermodynamic and mechanical properties are different. Clearly, the addition of 0.5% Co has modified the standard alloy substantially.

The change of characteristics produced by the cobalt addition can be summarized as follows:

- Hardness increase
- Tensile strength increase
- Reduction of hand workability
- Unchanged malleability
- Slight increase of the resistance to blanking
- Increased heat stability
- Easier control of heat treatment
- Unchanged appearance
- Slightly more expensive alloy.

In conclusion, the addition of 0.5% Co to the 5N standard 18 carat alloy does not reduce its range of use but gives a number of advantages that can counterbalance the slight increase of cost connected with the use of the modified alloy.

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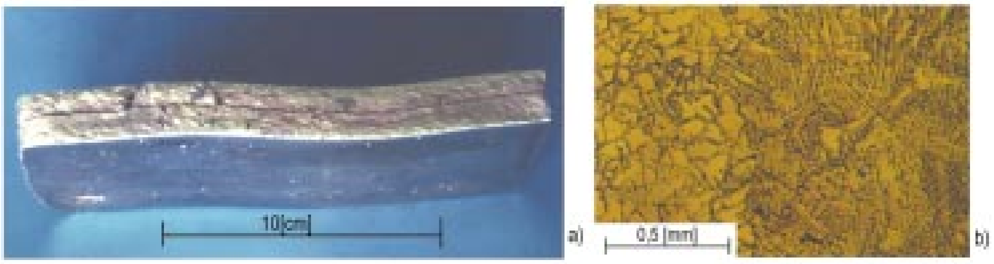

Figure 19 - a) Intergranular fractures in cold rolled 5N 0.5% Co alloy b) Alloy microstructure

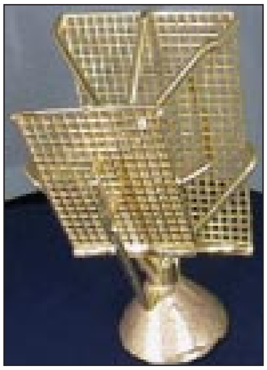

Figure 20 - Result of the investment casting test.